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Fate of Organophosphorus Insecticides in Soils. Part I. : The Retention of ^{32}P -Labeled Disulfoton and Dimethoate in the three Soils

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ratio of the methyl ketones and 3-methylbutanol in dairy products may be the determining factors of their attractancy for the mites, and that these attractants also may be one of the factors on the host selection of cheese mites.

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Summary

Besides methyl ketones, such as heptan-2-one, octan-2-one, nonan-2-one and 8-nonen-2-one, another attractive principle in cheddar cheese was identified. This was 3-methylbutanol, which showed the synergistic attractancy for the cheese mite, *Tyrophagus putrescentiae*, by mixing with the above methyl ketones. These components were considered to be important factors for the attractancy of dairy products to the cheese mite.

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Fate of Organophosphorus Insecticides in Soils. Part I. The Retention of ^{32}P -Labeled Disulfoton and Dimethoate in the three Soils. Ikuro KAWAMORI, Tetsuo SAITO and Kisabu IYATOMI (Laboratory of Applied Entomology and Nematology, Faculty of Agriculture, Nagoya University, Chikusa, Nagoya, Japan) Received December 19, 1970. *Botyu-Kagaku* 36, 7, 1971.

2. 有機燐殺虫剤の土壌施用に関する研究. 第1報 ^{32}P 標識 Disulfoton 及び Dimethoate の土壌における保持. 川森郁郎, 斎藤哲夫, 弥富喜三 (名古屋大学農学部害虫学教室, 名古屋市千種区不老町) 45. 12. 9. 受理.

^{32}P 標識 Disulfoton 及び Dimethoate の土壌による保持を沖積層土壌 (未耕地, 愛知県岡崎市), 頁岩風化土壌 (水田, 愛知県知多郡) 及び火山灰土壌 (畑地, 栃木県栃木農試) を用いて調べた.

土壌に施用した薬量と保持量との間には直線関係が見られ, Disulfoton は Dimethoate より多く土壌に保持された. また, 両薬剤に対する各土壌の保持量は火山灰土壌において最大であり, 頁岩風化土壌, 沖積層土壌の順であった. 保持薬量の多くが有機物の抽出方法で得られる画分に見い出され, 保持量は土壌の粘土含量よりむしろ有機物含量に密接な関連があるものと推論された.

薬剤と土壌構成物間の作用について薬剤の水溶性の相違から検討した.

Introduction

The application of systemic organophosphorus insecticides to soils offers an advantageous method of pest control because of their ecologically selective toxicities to the phytophagous insect

pests and labour saving for their application.

Most studies on the fate of pesticides in soils have been confined to chlorinated hydrocarbon insecticides and organic herbicides, and there are few reports on organophosphorus insecticides, especially systemic organophosphates. Since it is

generally accepted that the retention of insecticides applied to soils varies with nature of soils including biological factors, the basic information on the retention of systemic organophosphorus insecticides in various soils is necessary for their suitable application to soils. The present study was conducted in the laboratory to examine the initial retention of Disulfoton and Dimethoate in various soils.

Materials and Methods

Insecticides

³²P-labeled Dimethoate (*O,O*,-dimethyl *S*-(*N*-methylcarbamoyl methyl)phosphorodithioate) was synthesized by the method of Dauterman *et al* (1959).¹⁾ The synthesis of ³²P-labeled Disulfoton (*O,O*,-diethyl *S*-ethyl-2-mercaptoethyl phosphorodithioate) was done according to the methods of Metcalf *et al* (1957)²⁾ and O'Brien (1960).³⁾ The chemical and radiochemical purities of the insecticides were more than 90%. The specific radioactivities of Dimethoate and Disulfoton were about 600 c.p.m./ μ g and 400 c.p.m./ μ g respectively at the beginning of the experiments. These radiochemicals were stored as emulsifiable concentrates containing 47.5% benzene-acetone (1:1, w/w) and 2.5% Newcol 863 in a refrigerator at 5°C for 3 weeks, and diluted with distilled water just before application to the soils.

Soils

The three soils, loamy sand (uncultivated alluvial soil, Okazaki, Aichi Pref.), clay loam (paddy soil derived from tertiary shale, Chitagun, Aichi Pref.) and silty clay loam (field soil derived from volcanic ash, Utsunomiya, Tochigi Pref.) were air-dried, passed through a 2mm sieve and stored at room temperature. Their physico-chemical properties are listed in Table 1.

Application and Extraction Procedure

1) Each of the air-dried soils, 12.0g of loamy sand, 9.2g of clay loam or 5.6g of silty clay loam, was packed uniformly in a column with a glassfilter (2.0cm diameter) to a depth of 2.5cm. Ten milligrams of each insecticide were emulsified in 10ml of distilled water and applied to the soil column under suction. The column was washed with water (400ml) under suction to remove the non-retained insecticide until trace amount (less than 0.5% of initially applied amount) of radioactivity could be detected in the washing. The insecticide-retaining soil was transferred to an aluminium-foil dish, well mixed and weighed. Immediately after weighing, one ninth portion of the soil was placed in a planchet and dried up under an infrared lamp after adding 2 to 3 drops of 8% KOH methanol solution. The radioactivity of the insecticide retained in the soil was measured by Aloka thin window gas flow automatic counter. Self-absorption of radioactivity was corrected by weight.

2) Organic matter was extracted with a mixture of 0.1N NaOH and 0.1M Na₄P₂O₇ (1:1) according to the method of Kumada *et al* (1967).⁴⁾ One ninth portion of the insecticide-retaining soil was used for this extraction. The extract was separated from the residual soil by centrifugation at 4500 r.p.m. for 20 minutes. An aliquot of the supernatant was pipetted into a planchet and dried up by the same procedure as mentioned above. Organic carbon in the extract was determined by the method of Walkley and Black as described by Tatsukawa (1966).⁵⁾ The extraction with water was also done in parallel with that with the organic matter extractant.

3) The standard method⁶⁾ was adopted to separate clay (<2 μ) from one ninth portion of the insecticide-retaining soil, but hydrogen peroxide treatment for the decomposition of organic matter

Table 1. Physico-chemical characteristics of the soils.

Soils	Clay mineral	Organic matter ^{a)}	C. E. C. ^{b)}	pH (H ₂ O)	Soil moisture ^{a)}
loamy sand	1:1 type	1.1%	5.4	4.7	1.6%
clay loam	1:1 and 2:1 types	3.6	12.3	4.9	2.5
silty clay loam	allophane	15.5	33.2	5.3	7.3

a); The content as air-dried soil basis.

b); Cation exchange capacity as meq. per 100g of air-dried soil.

was conducted without heating. The clay suspension was separated from other soil components by pipetting and concentrated to about 10ml/ at $40 \pm 2^\circ\text{C}$ under reduced pressure. The clay suspension was then poured into a column with a glassfilter, on which a filter paper was previously fixed, under suction. The clay was collected into a planchet and dried up for the measurement of the radioactivity by the same procedure described above.

4) The degradation of Disulfoton was examined by alkali treatment. Ten ml of distilled water containing 10mg of Disulfoton was made over pH 10 with 6N KOH and allowed to stand at 25°C for 3 days. The degradation of Disulfoton was more than 90% under the present experimental condition. The degradation products were then applied to the soil after adjusting to the initial pH with 6N HCl. The retained amount in the

soil was measured by the same procedure as used for the retention of the insecticide in the soil.

Results and Discussion

The relations between amounts of the insecticides applied and these of retained were shown in Fig. 1. The amounts of the retained insecticides increased linearly with increase of their applied amounts to the soils. In every soil, Disulfoton was retained much more than Dimethoate. This result agreed with data reported by Graham-Bryce (1968)⁷⁾ with respect to the same toxicants. The amounts of the insecticides retained in silty clay loam, clay loam and loamy sand were about 7.8%, 3.1% and 1.2% of initially applied amounts of Disulfoton, and 0.23%, 0.09% and 0.05% of those of Dimethoate respectively. Larger amounts of the insecticides were retained in the soils having higher organic matter content and cation

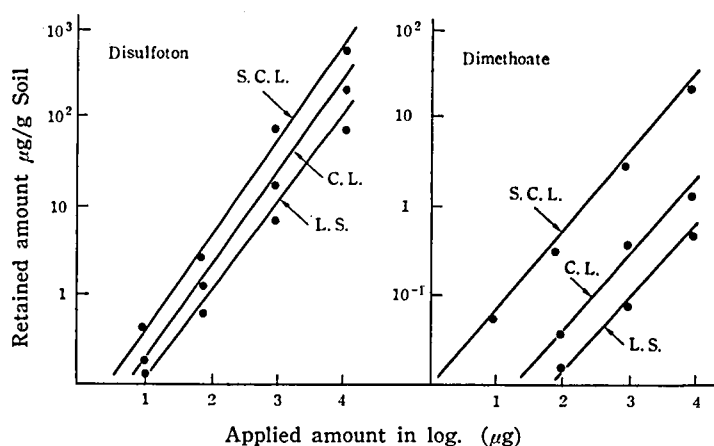


Fig. 1. The relations between applied and retained amounts of the insecticides in the soils. S.C.L.: silty clay loam, C.L.: clay loam, L.S.: loamy sand.

Table 2. The amounts of the radioactive materials in the fraction obtained by the organic matter extractant from the insecticide-retaining soils.

Soils	Disulfoton		Dimethoate	
	$\mu\text{g/g}$ air-dried soil ^{a)}	$\mu\text{g/mg}$ carbon ^{b)}	$\mu\text{g/g}$ air-dried soil ^{a)}	$\mu\text{g/mg}$ carbon ^{b)}
loamy sand	47.0	12.5	Trace	Trace
clay loam	200.0	15.4	Trace	Trace
silty clay loam	219.0	12.2	6.2	0.4

a) ; The radioactive materials extracted from one ninth portion of the insecticide-retaining soil were calculated as those extracted from 1g of air-dried soil.

b) ; Micrograms of the radioactive materials per mg carbon of the extracted organic matter.

exchange capacity. The retention of the insecticides seems to be related with organic matter content and/or cation exchange capacity of the soils.

Organic matter would appear to have a high potential adsorption capacity for pesticide, because many workers⁸⁻¹³⁾ have reported that the adsorption of pesticide by soil constituents correlated significantly to the content of organic matter rather than clay. The results presented in Table 2 indicate that the radioactive materials were recovered from the Disulfoton-retaining soils by the organic matter extractant in the following order; silty clay loam > clay loam > loamy sand, but no significant difference was observed among the values of μg of radioactive materials per mg of extracted organic carbon. It is therefore considered that the amount of the retained Disulfoton in the three soils is closely related to the content of their organic matter. On the other hand, the comparison of the amounts of the radioactive materials among the Dimethoate treated soils was unsuccessful, because the radioactivity extracted from the Dimethoate-retaining soils except silty clay loam was too small to measure.

The amount of the radioactivity in the fraction obtained by the organic matter extractant (0.1N

$\text{NaOH} + 0.1\text{M Na}_4\text{P}_2\text{O}_7$) was compared with that extracted with water. Table 3 showed that the difference of the ratios of the recovered radioactivity between both the extracts from Disulfoton-retaining loamy sand, clay loam and silty clay loam was 68.5%, 45.4% and 33.2% respectively, and 12.5% from the Dimethoate-retaining silty clay loam. In the case of Disulfoton, it is suggested that the different recovery of the radioactivity from the three soils is due to the different adsorptive strength of the insecticide to the soil components. Adsorption of the insecticides to the soil components also appears to depend on their physico-chemical properties and affinity for the adsorbents.

Concerning the adsorption of the insecticides to clay, much more amount of Disulfoton was found in clay fraction of silty clay loam than Dimethoate, but the amounts of the insecticides per mg of clay in the soils were smaller than those per mg of their organic matter (Tables 2, 4). Basing on the data shown in Tables 2 and 4, it is suggested that the amounts of the insecticides retained, especially Disulfoton, depend on the content of organic matter rather than clay in the three soils.

Table 3. The comparison of the recovered radioactivity from the insecticide-retaining soils by the organic matter extractant or water.

Soils	Extractant	Disulfoton (%)	Dimethoate (%)
loamy sand	0.1N $\text{NaOH} + 0.1\text{MNa}_4\text{P}_2\text{O}_7$ H_2O	100.0 31.5 ^{a)}	Trace
clay loam	0.1N $\text{NaOH} + 0.1\text{MNa}_4\text{P}_2\text{O}_7$ H_2O	100.0 54.6 ^{a)}	Trace
silty clay loam	0.1N $\text{NaOH} + 0.1\text{MNa}_4\text{P}_2\text{O}_7$ H_2O	100.0 66.8 ^{a)}	100.0 87.5 ^{a)}

a); Ratio (%) of the radioactivity in the extract by water to that by the organic matter extractant.

Table 4. The amounts of the insecticides found in the clay fraction of the soils.

Soils	Disulfoton		Dimethoate	
	$\mu\text{g/g}$ air-dried soil ^{a)}	$\mu\text{g/mg}$ clay ^{b)}	$\mu\text{g/g}$ air-dried soil ^{a)}	$\mu\text{g/mg}$ clay ^{b)}
loamy sand	20.8	0.4	Trace	Trace
clay loam	134.4	0.6	Trace	Trace
silty clay loam	152.6	0.7	56.3	0.3

a); The amount of the insecticide in clay separated from one ninth portion of the insecticide-retaining soil was calculated as that in clay included in 1 g of air-dried soil.

b); The amount of the insecticide per mg of clay extracted from the insecticide-retaining soil.

Table 5. Physical properties of the insecticides used.

Structural formula	Solubility in water at 20°C, m mole	Vapour pressure mm Hg
$\begin{array}{c} \text{C}_2\text{H}_5\text{O} \diagup \text{P} \begin{array}{c} \text{S} \\ \\ \text{S} \end{array} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{S} \cdot \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5\text{O} \diagdown \end{array}$ (Disulfoton)	5.3×10^{-2}	1.8×10^{-4} at 20°C
$\begin{array}{c} \text{CH}_3\text{O} \diagup \text{P} \begin{array}{c} \text{S} \\ \\ \text{S} \end{array} \text{CH}_2 \cdot \text{CONH} \cdot \text{CH}_3 \\ \text{CH}_3\text{O} \diagdown \end{array}$ (Dimethoate)	1.3×10^2	$< 10^{-4}$ at 25°C

Note: These values were compiled from technical data given by manufacturers and from Lord and Burt (1964).¹⁴⁾

On the initial retention of both the insecticides, it seems possible that the adsorption of the insecticides is influenced more effectively by weak physical binding such as van der Waals forces than by chemical binding such as cation exchange mechanisms, because the insecticides do not ionize and have relatively low polarity.

Several kinds of herbicides, as reviewed by Baily and White (1964),⁹⁾ appear to have the inverse relationship between their water solubility and adsorption to soils. Dimethoate is more soluble at about 2×10^3 times than Disulfoton in water, as shown in Table 5. On the contrary, Disulfoton was retained much more than Dimethoate in the soils (Fig. 1). It is suggested that the water solubility of both insecticides play an important role on their initial retention in the soils. Further observation, which was undertaken by alkali treatment of Disulfoton, revealed that the amounts of the degradation products retained in the soils were very small compared with those of Disulfoton itself (Table 6).

From the data obtained by the present study, it would be concluded that the initial retention

of the insecticides depends on the content of organic matter rather than clay in the soils, and correlates negatively with their water solubility.

Although the direct relations between the insecticides and the soil components were not studied in the present experiment, it is necessary to know such information on the relations, which are of importance for the application of organo-phosphorus insecticides to soils.

Summary

The relations between applied and retained amounts of ³²P-labeled disulfoton and dimethoate were studied by using the three soils.

The amounts of the retained insecticides increased linearly with their applied amounts to the soils. The retention of the insecticides was higher in disulfoton-treated soils than in dimethoate-treated ones. Both the insecticides were retained more in the order of silty clay loam, clay loam and loamy sand.

Most of the retained insecticides were found in the extractable organic matter fractions. The amounts of the retained insecticides were related to the content of organic matter rather than clay in the soils.

Interactions between the insecticides and the soil components were also discussed especially with reference to the water solubility of the insecticides.

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Table 6. The difference between the retention of Disulfoton and its degradation products to the soils.

Soils	Treated ^{a)} μg/g air-dried soil	Untreated μg/g air- dried soil
loamy sand	16.6	120.0
clay loam	20.3	310.0
silty clay loam	32.4	780.0

a); Alkali treatment of disulfoton. See further explanation in Materials and Methods.

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Fate of Organophosphorus Insecticides in Soils. Part II. The Changes of the Retention and the Metabolism of ^{32}P -Labeled Disulfoton and Dimethoate in the Soils. Ikuro KAWAMORI, Tetsuo SAITO and Kisabu IYATOMI (Laboratory of Applied Entomology and Nematology, Faculty of Agriculture, Nagoya University, Chikusa, Nagoya, Japan) Received January 9, 1971. *Botyu-Kagaku* 36, 12, 1971.

3. 有機磷殺虫剤の土壤施用に関する研究。第2報 ^{32}P 標識 Disulfoton 及び Dimethoate の土壌における保持及び代謝の経時的変動。川森郁郎, 斎藤哲夫, 弥富喜三 (名古屋大学農学部害虫学教室, 名古屋市千種区不老町) 46. 1. 9. 受理。

^{32}P 標識 Disulfoton 及び Dimethoate の湛水土壌における保持と代謝の経時的変動を調べた。

施用直後に土壌に保持された Disulfoton の量は Dimethoate より多く、特に火山灰土壌では他の土壌より多量に保持された。また、Disulfoton を施用した土壌による放射活性の保持は時間の経過に伴ない漸次増加した。一方、施用直後における Dimethoate の土壌による保持量は非常に少なかったが施用後2日間で急激に増加した。

土壌有機物抽出法で得られる抽出液中の放射活性は Dimethoate 保持の土壌よりも Disulfoton 保持の土壌で高く、それらの値は時間の経過に伴なって増加した。

Dimethoate を施用した土壌からの水溶出物中から得られるクロロホルム可溶物質 (加水分解を受けていない物質及び誘導体) の相対量は Disulfoton を施用した土壌からのそれより多かった。しかし、それらの相対量の土壌間での差は Disulfoton を施用した土壌で見られ沖積土壌>頁岩風化土壌>火山灰土壌の順であったが、Dimethoate を施用した土壌間では明らかな差が見られなかった。Disulfoton 施用後10日経過した土壌からの水溶出物中から得られるクロロホルム画分に Disulfoton の sulfoxide 誘導体が出された。また、Disulfoton の相対量が減少する一方、Disulfoton thiol 化合物の sulfone 体が増加した。しかし、Disulfoton 及び Dimethoate の thiol 化合物は本実験条件下では検出されなかった。

Introduction

Systemic insecticides can be applied in various ways: foliar spray, bark, seed and soil treatments, etc. In soil application, most of the insecticides

may have no direct contact to plant roots, and their behaviours are affected by water flow in soils and nature of soils. It is therefore important to investigate the interaction between soil and insecticide in order to get informations on the